

# Post-mortem analysis of radiation grafted fuel cell membrane using X-ray photoelectron spectroscopy

Mohamed Mahmoud Nasef<sup>a</sup> \*and Hamdani Saidi<sup>b</sup>

<sup>a</sup> Chemical Engineering Program, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia

<sup>b</sup> Membrane Research Unit, Universiti Teknologi Malaysia, Jalan Semarak, 54100 Kuala Lumpur, Malaysia.

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**Abstract:** A post-mortem analysis of poly(tetrafluoroethylene-co-perfluorovinyl ether)-graft-polystyrene sulfonic acid (PFA-g-PSSA) membrane was carried out at the end of polymer electrolyte membrane (PEM) fuel cell test using X-ray photoelectron spectroscopy (XPS). The membrane was prepared by radiation-induced grafting of styrene onto PFA film using simultaneous irradiation technique followed by sulfonation reaction. The membrane was initially analyzed in its virgin state and the obtained data was used as a reference. The XPS results showed that the used membrane has undergone substantial structural changes, particularly in terms of chemical composition and concentration of its basic elemental components (Carbon, fluorine, oxygen and sulfur) as a result of degradation. This was found to be mainly due to the decomposition of polystyrene sulfonic side chain grafts. These results were confirmed by FTIR spectral analysis. It can be suggested that the oxidative degradation taking place in the PFA-g-PSSA membrane during fuel cell test is mostly due to the chemical attack at the tertiary hydrogen of  $\alpha$ -carbon of polystyrene side chain grafts. Moreover, XPS can be proposed as an effective tool for monitoring membrane degradation after fuel cell experiments.

**Key words :** Post-mortem analysis, radiation grafted PFA-g-PSSA membrane, PEM fuel cell, XPS.

## 1. INTRODUCTION

The growing demand for high quality and cost-effective proton exchange membranes for polymer electrolyte membrane (PEM) fuel cells has derived many research efforts towards the development of new membrane materials [1]. Radiation grafted membranes bearing sulfonic acid groups are among the proposed alternative candidates [2,3]. Compared to other newly developed materials, these membranes have the advantages of well-controlled composition and properties through proper selection of grafting parameters, no shaping problem due to the use of commercial polymer films and low cost [4-6]. Due to the chemical stability needed in PEM fuel cells, these membranes are commonly prepared by radiation grafting of styrene or its derivatives onto various fluorinated polymer films followed by a sulfonation reaction [1,2].

Commercial and experimental radiation grafted sulfonic acid membranes based on polytetrafluoroethylene (PTFE), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), and poly(tetrafluoroethylene-*alt*-ethylene) (ETFE) were tested in PEM fuel cell and showed stability up to 1000-1400 h [5-7]. However, one of the major problems that have to be circumvented to promote the practical application of these membranes is the oxidative degradation under the influence of chemical attack by hydroproxy radicals produced at the anode during the PEM fuel cell operation [8]. A membrane lifetime of at least 5000 h is desired for commercial applications.

Despite the high significance of the issue of membrane degradation from the beginning, yet little information has been published in literature. The early work addressing the degradation of polystyrene sulfonic acid (PSSA) membranes in a simulated fuel cell environment using PSSA resin was reported by Hodgson et al. three decades ago [9]. The degradation was suggested

\*To whom correspondence should be addressed: Fax: + 605 3721111;  
e.mail: mahmoudeithar@mailcity.com

to be due to two factors; weak links such as (-O-O-) in PSSA backbone and the oxidative attack on the tertiary hydrogen of  $\alpha$ -carbon. This was supported by the first data published ten year later on the degradation of divinylbenzene crosslinked PSSA membranes, which showed that more degradation is likely to occur at the anode side as a result of oxygen diffusion [8]. The replacement of hydrocarbon substrates by fluorinated ones has improved the chemical stability of PSSA membranes remarkably. Nevertheless, recent investigations showed that fluorinated PSSA membranes remain vulnerable for chemical attack [2, 6, 10, 11]. Büchi et al. evaluated the degradation of FEP-g-PSSA membranes after a long-term stability test in PEM fuel cell by monitoring the loss of ion exchange capacity along with FTIR spectral analysis. Mattson et al. studied the degradation of polyvinylidene fluoride-graft-polystyrene sulfonic acid (PVDF-g-PSSA) membrane after a PEM fuel cell test using confocal Raman spectroscopy [11].

The objective of the present study is to address the fuel cell membrane degradation problem using XPS technique. The selection of XPS was made after it was effectively applied to study structural changes taking place in various fluorinated radiation grafted sulfonic acid membranes, prepared in our laboratory, in correlation with preparation procedure (grafting and sulfonation) and variation of the degree of grafting [12-14]. PFA-g-PSSA membrane is selected for this study where it is investigated before and after PEM fuel cell experiment to monitor the structural changes taking place under the influence of oxidative degradation. A study of such kind may help in understanding the degradation mechanism of PFA-g-PSSA membranes during the ongoing fuel cell tests and the subsequent necessary precautions to be undertaken to enhance the stability.

## 2. EXPERIMENTAL

### 2.1 Membrane Preparation

PFA-g-PSSA membrane (16% degree of grafting) was prepared using a two-step procedure as reported earlier [15,16]. In the first step, PFA film (120  $\mu\text{m}$  thick) (Porghof) was grafted with styrene diluted with dichloromethane (30/70 v:v) using simultaneous irradiation technique. The grafting mixture was placed in tightly sealed glass ampoule and irradiated to a total dose of 20 kGy for 15 h using  $\gamma$ -rays from a  $^{60}\text{Co}$  source (located at Malaysia Institute for Nuclear Technology Research) under nitrogen atmosphere at room temperature. The grafted film was thoroughly washed with toluene several times and dried under vacuum. In the second step, the grafted PFA film was sulfonated using a chlorosulfonic acid/1,1,2,2-tetrachloroethane mixture (30/70 v:v) at a temperature of 90 °C for 5 h. A degree of sulfonation of 96 % was achieved. The degree of grafting was calculated as the percent of weight increase in the grafted film with respect to the weight of the original PFA film. The membrane performance was tested in a single fuel cell (Globe Tech., Inc.)

having a geometric area of 5  $\text{cm}^2$  and running with pure  $\text{H}_2$  (humidified at 70°C) and  $\text{O}_2$  (humidified at 65°C) gases at constant temperature of 50 °C. The wet membrane was assembled with two reference electrodes (E-TEK) by placing the three components between two stainless steel blocks (each weighing 5 kg) for 48 hours at 50 °C without any special treatment. This step was taken to easily peel the electrodes from the membrane without causing damage to either component. At the end of the fuel cell test (few hundred hours) the membrane was carefully removed, cleaned with boiled water and then vacuum dried.

### 2.2 XPS Measurements

XPS measurements were conducted using Kratos XSAM-HS surface micro analyzer having a Mg  $\text{K}_{\alpha}$  x-ray source (1253.6 eV) in Fixed Analyzer Transmission (FAT) mode. The instrument was calibrated using pure silver plate giving Ag  $3d_{5/2}$  at 368.25 eV and  $\Delta \text{Ag} = 6.00$  eV. Low x-ray flux of the non-monochromatized Mg  $\text{K}_{\alpha}$  line normally operated at 10 mA and 12 kV was used, while charge neutralizer was switched on to minimize the charging effect. Binding energies of all photoelectron effects were corrected by deducing the charging effect values based on C1s at 284.5 eV for terminal hydrocarbon ( $-\text{C}_{\alpha}-$ ). The Gaussian peak fitting parameter with straight baseline was applied for peak analysis using Vision software supplied by Kratos. The elemental composition of the top layers of the membrane samples was directly retrieved from the XPS scans, whereas the bulk structural properties were obtained using in-situ sputtering by argon gas. Surface and bulk investigations were conducted on the virgin and used membranes along with corresponding pre-grafted and grafted PFA films.

### 2.3 FTIR Measurements

FTIR measurements were carried out using a Nicolet (Magna-IR 560) spectrometer equipped with ATR (Thunder dome-HATR) having Germanium spherical crystal. The spectra were measured in transmittance mode at a wave number range of 4000-600  $\text{cm}^{-1}$  and analyzed using commercial software.

## 3. RESULTS AND DISCUSSION

PFA-g-PSSA membrane having 16 % degree of grafting was prepared styrene grafting and subsequent sulfonation. A general molecular structure of PFA-g-PSSA membrane is given in Figure 1. The membrane quality was determined by evaluating its various properties. A summary of the physico-chemical properties of the membrane is presented in Table 1. The selection of a membrane with 16 % degree of grafting is based on the high possibility of achieving a homogeneous graft distribution [16]. This was confirmed by XPS spectral analysis, which was taken from both membrane sides and found to be identical illustrating the presence of a symmetrical structure [12]. The membrane was tested in fuel cell for few hundred hours under

the present experimental conditions. The performance of the membranes after the first 50 h is shown in Figure 2. The low performance of the fuel cell is mainly attributed to the ohmic loss resulting from the high contact resistance as the membrane was assembled with the electrodes without hot pressing and liquid electrolyte impregnation.

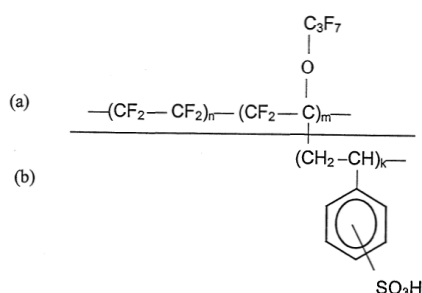


Figure 1: General molecular structure of PFA-g-PSSA membrane.

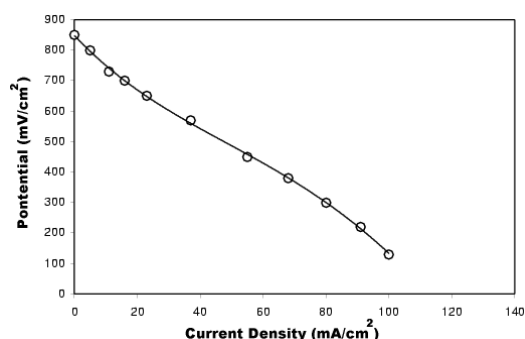


Figure 2: Polarization curve of PEM fuel cell for PFA-g-PSSA membrane after first 50 h of operation.

Table 1: Summary of the physico-chemical properties of 16 % grafted PFA-g-PSSA membrane.

Properties	Value
Thickness	$160 \pm 2 \mu m$
Ion exchange capacity	$1.6 \pm 0.2 \text{ meq/g}$
Water uptake	$27 \pm 0.5 \text{ wt \%}$
Hydration number	$10 \pm 1$
Proton conductivity.	$3.3 (\pm 0.5) \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$

To understand the nature of the degradation process and its location in the membrane, it is important to monitor the chemical structure (composition and concentration of each elemental component) built up during the membrane preparation (grafting and sulfonation) in a preliminary step. This was carried out

by comparing XPS investigation of the membrane with similar analysis for original and 16 % grafted (pre-sulfonated) PFA films. Table 2 shows quantitative analysis of elemental components of 16 % grafted PFA-g-PSSA membrane compared to original and grafted PFA films as obtained from the wide scan XPS spectra. The F/C ratio in the original film is found to be 2.29, whereas that of O/C ratio equals 0.27. Both values are higher than their respective theoretical ones obtained from the chemical structure of tetrafluoroethylene perfluorovinyl ether copolymer in which F/C and O/C equal 2.00 and 0.14, respectively [13]. The high value of F/C ratio in original PFA film indicates that fluorine atoms are somewhat concentrated on its surface. Whereas, the high value of O/C is mostly due to a contamination with oxygen coming from additives such as fillers (e.g. fibre glass), which are often added to fluorinated polymers to facilitate the film shaping and improve their mechanical properties [17]. This observation indicates that polymer backbone elemental components i.e. fluorine and carbon have a very significant role to play during the membrane preparation and are expected to do so during degradation.

The results in Table 2 obviously show that PFA film undergoes substantial structural changes in terms of chemical composition and concentration of its basic elements under the influence of styrene grafting and subsequent sulfonation. Grafting is found to increase the hydrocarbon fraction at the expense of fluorine domain, particularly at the membrane surface. For instance, the F/C ratio dropped to 0.16. This is a result of drastic reduction in the fluorine content by the consumption of C-F bonds in formation of radicals required to initiate the graft copolymerization reactions. Moreover, O/C ratio was declined to 0.13. Sulfonation resulted in a further reduction in the fluorine content (F/C ratio slipped to 0.09) and emergence of a new elemental component i.e. sulfur, coupled with an increase in the oxygen concentration (O/C ratio hiked to 0.21). This indicates that the incorporated oxygen rich sulfonic acid groups are mostly concentrated near the surface of the membrane. Similar results were reported for a commercial PTFE-g-PSSA membrane (Permion 4010, RAI, USA) using x-ray microprobe analyzer [2]. The PTFE-g-PSSA membrane was prepared using similar procedure to that in the present work (simultaneous grafting of styrene followed by sulfonation) [2]. It can be concluded that the PFA-g-PSSA membrane composes of 4 basic elemental components i.e. carbon, fluorine (mainly representing film backbone), oxygen and sulfur (representing functional groups). Therefore, determination of the locus of degradation in PFA-g-PSSA membranes after PEM fuel cell test requires clear recognition of the changes taking place in these four elements.

Figure 2 shows a survey wide scan spectrum of virgin and used PFA-g-PSSA membranes having a degree of grafting of 16 %. Four characteristic peaks at 284.5, 531.8, 688.8 and 168.2 eV were detected in spectrum A (Fig. 2) of the virgin membrane. These peaks were assigned for C 1s, F 1s, O 1s and S 2p of

Table 2: Quantitative analysis of the basic elemental components of PFA-g-PSSA membrane compared to original and grafted PFA films.

Sample	Atomic concentration(%)			
	C	F	O	S
Original PFA film	27.8	63.7	7.5	-
16 % grafted PFA film	77.5	12.5	10.5	-
PFA-g-PSSA membrane	76.6	6.7	16.1	2.8

the basic elemental components of the membrane, respectively. Compared to virgin membrane, the spectrum of the used one (Figure 2 B) shows that the membrane undergoes significant changes in terms of chemical composition of its basic elemental components under the influence of oxidative degradation. For instance, only three characteristic peaks corresponding to C 1s, F1s, O1s at 284.5, 689.1 and 532.0 eV were identified. The S2p peak (representing sulfur) that was previously located at 168.2 eV (spectrum A) disappeared from the used membrane spectrum. Coincidentally, a remarkable decrease in the intensity of O 1s took place. Moreover, the intensity of F 1s was found to increase drastically whereas that of C 1s was sharply declined leading to an increase in the ratio of F/C from 0.09 in the virgin membrane to 1.10 in the used one. The simultaneous loss of sulfur and the oxygen reduction suggest that a complete removal of sulfonic acid groups from the membrane took place. This was confirmed from the narrow scan and the curve fitting of O 1s of virgin and used PFA-g-PSSA membranes as shown in Figure 3. The O 1s spectrum of the virgin membrane was deconvoluted into four corrected peaks at 534.3, 532.9, 531.5 and 529.8 eV (charging effect = 1.5 eV) as depicted in Figure 3 (A). The peak at a 529.8 eV was assigned for the oxygen present in sulfonic acid group ( $\text{-S=O}$ ) and the other three ones were assigned for oxygen from various sources such as O-H of water,  $\text{-O-}$  of ether group and  $\text{=O}$  of ( $\text{C=O}$ ), respectively. In comparison, the O1s spectrum of the used membrane depicted in Figure 3 (B) shows only three binding energy peaks (corrected) at 534.3, 532.9 and 531.5 eV (charging effect = 2.0 eV) representing O-H of water,  $\text{-O-}$  of ether group and  $\text{=O}$  of ( $\text{C=O}$ ). The complete disappearance of the binding energy peak of  $\text{S=O}$  at 529.8 eV is a strong evident for elimination of sulfonic acid groups from the used membrane.

To determine the changes occurred in the carbon and fluorine under the influence of membrane oxidative degradation, further analysis by narrow scanning of C1s spectra of both virgin and used membranes was carried out. Figure 4 shows a narrow scan of C 1s of the virgin and used PFA-g-PSSA membranes. A predominant C 1s peak at 284.5 eV binding energy of the hydrocarbon component [C (H)] in companion with a very weak peak for C 1s at 291.8 eV (corrected) binding energy (charging effect = 2.4 eV) of the fluorocarbon component can be clearly seen

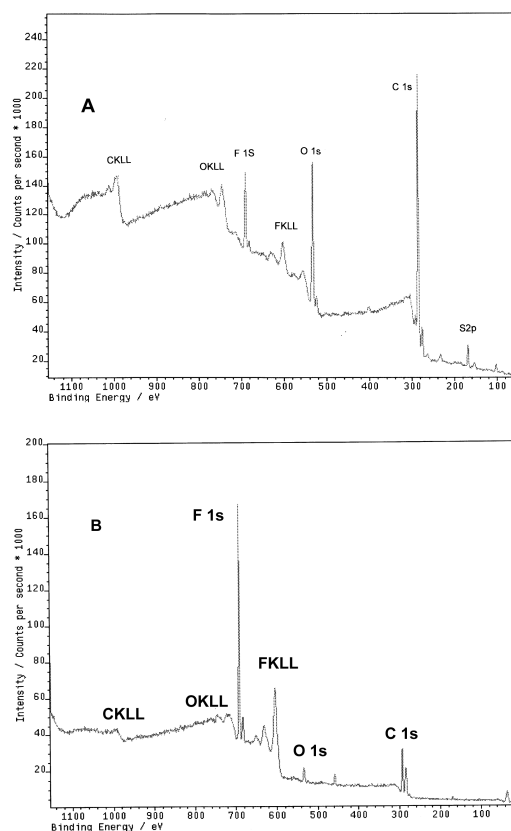


Figure 3: Survey wide scan spectrum of: (A) virgin PFA-g-PSSA membrane; (B) used PFA-g-PSSA membrane.

in the C 1s spectrum of the virgin membrane as shown in Figure 4 (A). In addition, a small satellite peak due to  $\pi\text{-}\pi^*$  (band to band) losses can be hardly observed at 288.6 eV (corrected) confirming the presence of polystyrene [18]. The relative intensity of C 1s at 284.5 eV to C 1s at 291.8 eV is found to be 1/100. The separation of the two peaks by 7.3 eV which, is due the chemical shift under the influence of electron attraction towards fluorine atom, is in a good agreement with the literature [19]. The spectrum of the used membrane shown in Figure 4 (B), reveals an opposite trend. For instance, the peak of C (F) at 291.8 eV (charging effect = 3.5 eV) is dramatically increased whereas correct C (H) at 284.5 eV is sharply reduced. These results indicate that the oxidative chemical attack is taking place on the hydrocarbon fraction of the membrane i.e. the grafted polystyrene sulfonic acid moieties.

To further investigate the impact of the chemical attack on the grafted hydrocarbon fraction of the membrane, a curve fitting of C 1s spectrum was carried out. Figure 5 shows curve fitting of C1s spectra of virgin and used PFA-g-PSSA membranes. The C1s spectrum of the virgin membrane (Figure 5 A) is deconvoluted into five peaks having corrected binding energies of 292.8,

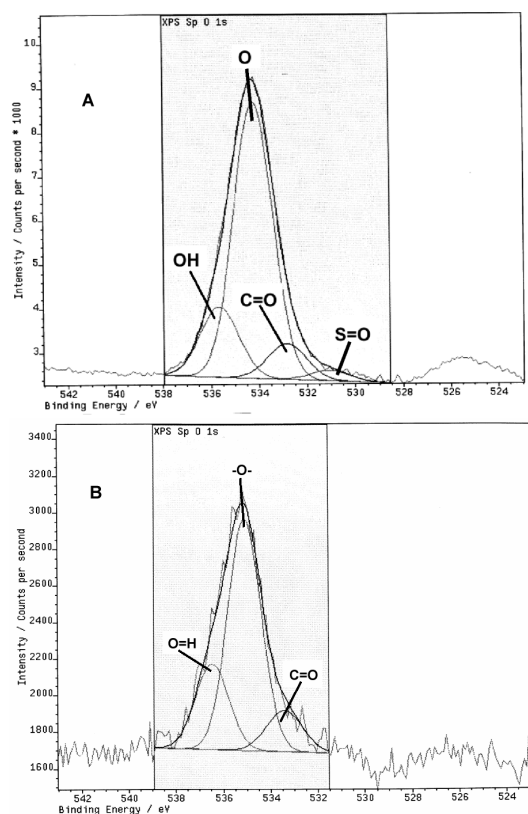


Figure 4: Narrow scan and curve fitting of O1s of: (A) virgin PFA-g-PSSA membrane; (B) used PFA-g-PSSA membrane.

288.9, 287.3, 285.6 and 284.5 eV (charging effect = 1.2 eV), which are assigned for  $\text{CF}_2$ ; C-S; C-O or C-CF;  $-\text{C}_\beta-$  and  $\text{C}_\alpha-$ , respectively. The dominance of the  $-\text{C}_\beta-$  and  $\text{C}_\alpha-$  belonging to the hydrocarbon component (sulfonated polystyrene) in the membrane, can be obviously seen. Moreover, a very small amount (relative intensity of  $\text{C}_F/\text{C}_{\text{total}} = 4.7\%$ ) of fluorine ( $\text{CF}_2$ ) of PFA backbone is recorded in the membrane surface. Removing of surface layers by in-situ sputtering is found to bring fluorine content in the membrane surface towards higher values (nearly 19 %) with the emergence of two new fluorine-containing peaks representing CF and  $\text{CF}_3$ . These results reveal that the membrane surface is dominated by the pure hydrocarbon fraction and this is in a complete agreement with the literature [20]. The difficulty in the specific determination of  $-\text{C}_\beta-$  and  $\text{C}_\alpha-$  of aliphatic ( $-\text{CH}_2-\text{CH}=-$ ) and aromatic ( $-\text{C}_6\text{H}_4$ ) of sulfonated polystyrene incorporated in the grafted film is due to the minor chemical shifts in these carbon atoms [20]. Unlike, C 1s of the virgin membrane, the deconvolution of C 1s of the used membrane showed two additional peaks (corrected) at 295.5 and 293.2 eV (charging effect = 0.5 eV) representing  $\text{CF}_3$  and CF as depicted in Figure 5 (B). The appearance of  $\text{CF}_3$  and CF peaks again is a strong indication for the removal of

hydrocarbon fraction from the membrane.

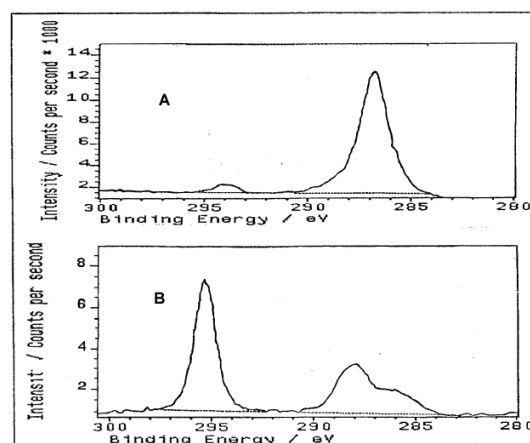


Figure 5: Narrow scan of C1s of: (A) virgin PFA-g-PSSA membrane; (B) used PFA-g-PSSA membranes.

These results were supported by the quantitative values of atomic concentrations and ratios of the elemental components of the used membrane when compared with those of the virgin one as presented in Tables 3 and 4, respectively. The data indicates that a great part of polystyrene was removed from the membrane surface under the influence of oxidative degradation allowing the emergence of previously covered minor fluorine components ( $\text{CF}_3$  and CF). Accordingly, it can be suggested that the used membrane surface is no longer dominated by the hydrocarbon component, mostly due to the decomposition of polystyrene side chain grafts took place at tertiary-hydrogen of  $\alpha$ -carbon. Moreover, a fluorinated structure similar to the pre-grafted (original) PFA film is most likely left. These results were further confirmed by FTIR spectral analysis of both virgin and used membranes as shown in Figure 6. The disappearance of the bands at 1128, 1034 and  $1006\text{ cm}^{-1}$  from the spectrum of the used membrane (A) compared to that of the virgin one (B) is a strong evident for the complete removal of the  $\text{SO}_3^-$  groups. This was accompanied by the disappearance of the aromatic ring features such as the skeletal C=C in plate-stretching vibrations at 1493 and  $1602\text{ cm}^{-1}$  and C-H aromatic stretching vibrations at  $3026\text{ cm}^{-1}$  along with the sharp decrease in the aliphatic C-H stretching vibrations peaks at 2925 and  $2854\text{ cm}^{-1}$ , respectively. It can be finally concluded that the oxidative degradation taking place in the PFA-g-PSSA membrane during the PEM fuel cell operation is located in the hydrocarbon fraction represented by sulfonated polystyrene side chain grafts. The chemical attack by hydroxy radicals mostly occurs on the vulnerable tertiary hydrogen of the  $\alpha$ -carbon causing the termination of the whole sulfonated polystyrene grafts. These results are in good agreement with those reported in literature [6,11].

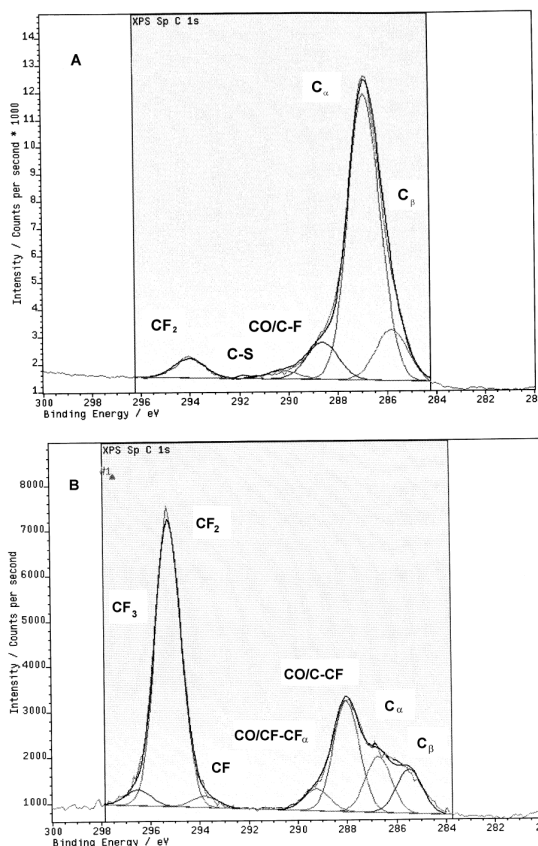


Figure 6: Curve fitting of C1s of: (A) virgin PFA-g-PSSA membrane; (B) used PFA-g-PSSA membrane.

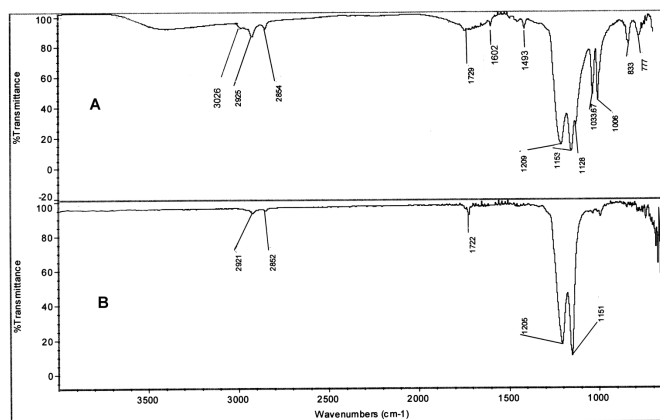


Figure 7: Typical FTIR spectra of: (A) virgin PFA-g-PSSA membrane; (B) used PFA-g-PSSA membrane.

Table 3: Atomic concentrations of the basic elemental components of the used PFA-g-PSSA membrane compared to those of the virgin one.

Sample	Atomic concentration			
	C 1s	F 1s	O 1s	S 2p
Used membrane	45.4	51.8	4.8	0
Virgin membrane	76.6	6.7	16.1	2.8

Table 4: Atomic ratios of the basic elemental components of the used PFA-g-PSSA membrane compared to those of the virgin one.

Sample	Atomic ratio)			
	F/C	S/C s	O/C	O/S
Used membrane	1.10	0.00	0.10	0.00
Virgin membrane	0.10	0.04	0.26	2.80

It should be pointed out that degradation of water soluble polystyrene sulfonic acid (PSSA) originated from homopolymer (non-bound) is expected to significantly contribute to the overall membrane degradation as it was produced using simultaneous irradiation technique. Further research is needed to differentiate the degradation taking place due to the decomposition of grafted polystyrene sulfonic acid chains from the leaching of ungrafted sulfonated polystyrene. Additional morphological investigations with x-ray microprobe analyzer to screen the structural changes in the various layers from surface to surface (depth profile analysis) would also assist in drawing a precise degradation mechanism for PFA-g-PSSA membranes during the PEM fuel cell operation.

#### 4. CONCLUSION

XPS spectral analysis was found to be very useful technique for studying membrane degradation after fuel cell test. Structural changes resulted from oxidative degradation of PFA-g-PSSA membrane was qualitatively and quantitatively monitored in terms of chemical composition and basic elemental concentration. The used membrane was found to have no sulfur and less oxygen compared to the virgin one. This provides a strong evidence for the complete elimination of the sulfonic acid groups from the membrane. The dramatic decrease in hydrocarbon content coupled with the increase in the fluorine fraction confirmed by emergence of new fluorine peaks reveals that polystyrene side chain grafts were also substantially decomposed. The overall result of this work suggests that membrane oxidative degradation during PEM fuel cell test is due to the decomposition of sulfonated polystyrene side chain grafts as a result of chemical attack at the tertiary hydrogen of  $\alpha$ -carbon.

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